

On bound state computations in three- and four-electron atomic systems

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Abstract

A variational approach is developed for bound state calculations in three- and four-electron atomic systems. This approach can be applied to determine, in principle, an arbitrary bound state in three- and four-electron ions and atoms. Our variational wave functions are constructed from four- and five-body gaussoids which depend upon the six $(r_{12}, r_{13}, r_{14}, r_{23}, r_{24}, r_{34})$ and ten $(r_{12}, r_{13}, r_{14}, r_{15}, r_{23}, r_{24}, r_{25}, r_{34}, r_{35}$ and $r_{45})$ relative coordinates, respectively. The approach allows one to operate with the different number of electron spin functions. In particular, the trial wave functions for the 1S -states in four-electron atomic systems include the two independent spin functions $\chi_1 = \alpha\beta\alpha\beta + \beta\alpha\beta\alpha - \beta\alpha\alpha\beta - \alpha\beta\beta\alpha$ and $\chi_2 = 2\alpha\alpha\beta\beta + 2\beta\beta\alpha\alpha - \beta\alpha\alpha\beta - \alpha\beta\beta\alpha - \beta\alpha\beta\alpha - \alpha\beta\alpha\beta$. We also discuss the construction of variational wave functions for the excited 2^3S -states in four-electron atomic systems.

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I. INTRODUCTION

In this study we consider the electronic structure of three- and four-electron atoms and ions. In particular, we undertake variational computations of the singlet 1S -states and triplet 3S -states in various four-electron atoms and ions. Below, by an atomic system we mean a system which contains a number of electrons and one heavy nucleus. In the non-relativistic approximation used in this study the Hamiltonian of an arbitrary $(A - 1)$ -electron atomic system takes the form (see, e.g., [1])

$$H = -\frac{1}{2}\left[\sum_{i=1}^{A-1}\nabla_i^2 + \frac{1}{M}\cdot\nabla_A^2\right] - \sum_{i=1}^{A-1}\frac{Q}{r_{iA}} + \sum_{i=1}^{A-2}\sum_{j=2(>i)}^{A-1}\frac{1}{r_{ij}} \quad (1)$$

where A is the total number of bodies in the atomic system. In a three-electron atomic system one has $A = 4$ in Eq.(1). In this case the subscripts 1, 2, 3 designate three electrons, while the subscript 4 denotes the positively charged atomic nucleus. For four-electron systems we have $A = 5$ in Eq.(1) and the subscripts 1, 2, 3, 4 designate four electrons, while the subscript 5 denotes the positively charged nucleus. Note that the Hamiltonian, Eq.(1), and all equations that follow are written in atomic units, where $\hbar = 1, m_e = 1, e = 1$. Also, in Eq.(1) $\nabla_i = (\frac{\partial}{\partial x_i}, \frac{\partial}{\partial y_i}, \frac{\partial}{\partial z_i})$ is the gradient operator of the i -th particle ($i = 1, 2, \dots, A$). The notation r_{ij} stands for the (ij) -relative distance/coordinate between i -th and j -th particles, i.e. $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j| = r_{ji}$, where \mathbf{r}_i are the Cartesian coordinates of the i -th particle. Also, in Eq.(1) the notation M stands for the mass of the central (heavy) nucleus, i.e. $M \gg 1$.

The main goal of this work is to discuss some important details of bound state calculations of three- and four-electron atoms and ions. In particular, special attention will be given to the correct symmetrization of the four-electron trial wave functions which include more than one independent (electron) spin function, something not considered elsewhere in the modern literature. Formally, our main goal is to determine highly accurate solutions of the Schrödinger equation $H\Psi = E\Psi$ where H is the Hamiltonian, Eq.(1), while E is the eigenvalue (= total energy) of the considered bound state and Ψ is the corresponding wave function. It is clear that the permutation symmetry of the total wave function Ψ must be different for the singlet and triplet bound states in four-electron system. The explicit construction of trial wave functions with the correct permutation symmetry between all three or all four electrons is the principal part of any accurate variational calculation of such

atomic systems.

In general, bound state computations of three-, four- and many-electron atomic systems with the use of a number of different spin functions (which, however, correspond to the same value of the total (electron) spin S_e and its z -projection $(S_e)_z$) are significantly more complicated than analogous calculations for two-electron helium-like atoms and ions. On the other hand, there is an obvious similarity in calculations of three- and four-electron atomic systems. Indeed, for the ground (doublet) 1^2S -states in three-electron atoms and ions one needs to use the two different spin functions. The same number of spin functions is needed for accurate computations of the 1^1S -states in four-electron atomic systems.

Note that in any four-electron atom and/or ion all bound states are separated into two series of states: singlet states with the total electron spin S_e equals zero, i.e. $S_e = 0$; and triplet states with the total electron spin S_e equals unity, $S_e = 1$. In all previous works only the ground singlet 1^1S -state was considered. Accurate computations of the triplet states in four-electron atomic systems have been performed for a very few ions/atoms [2], [3]. Moreover, in almost all previous computations of the singlet state in four-electron (Be-like) atoms and ions only one spin function $\chi_1 = \alpha\beta\alpha\beta + \beta\alpha\beta\alpha - \beta\alpha\alpha\beta - \alpha\beta\beta\alpha$ was used. Here and everywhere below in this study α and β are the spin-up and spin-down single electron functions, i.e. $\hat{\sigma}_z\alpha = \frac{1}{2}\alpha$ and $\hat{\sigma}_z\beta = -\frac{1}{2}\beta$. The second independent spin function $\chi_2 = 2\alpha\alpha\beta\beta + 2\beta\beta\alpha\alpha - \beta\alpha\alpha\beta - \alpha\beta\beta\alpha - \beta\alpha\beta\alpha - \alpha\beta\alpha\beta$ has been ignored in almost all modern accurate computations of the singlet states in four-electron atomic systems. Bearing this in mind we wanted to develop the method which can be used to perform bound state computations for the 1^1S -singlet and 3^1S -triplet bound states in arbitrary four-electron atoms and ions. Our method is not restricted with respect to the number of spin functions included. It works equally well in cases, when one, two, three and even more independent spin functions are used.

II. VARIATIONAL WAVE FUNCTIONS

A central feature of any variational method is the construction of trial wave functions Ψ with the correct permutation symmetry. In general, such a trial wave function must include all electron and nuclear coordinates. Accurate wave functions explicitly depend upon all scalar interparticle coordinates $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ in the atomic system. The use of a large number

of relative coordinates complicates the explicit symmetrization of the trial wave functions. Another complication follows from the presence of different (independent) terms in the spin part of the total wave function. For instance, let us discuss the case of the singlet 1S -state in four-electron atomic systems. To compute this state in this study we shall use the two following independent spin functions written in the form $\chi_1 = \alpha\beta\alpha\beta + \beta\alpha\beta\alpha - \beta\alpha\alpha\beta - \alpha\beta\beta\alpha$ and $\chi_2 = 2\alpha\alpha\beta\beta + 2\beta\beta\alpha\alpha - \beta\alpha\alpha\beta - \alpha\beta\beta\alpha - \beta\alpha\beta\alpha - \alpha\beta\alpha\beta$. These two functions obey the following relations

$$\mathbf{S}^2\chi_k = 0 \quad , \quad (\mathbf{S}_z)\chi_k = 0 \quad , \quad \langle \chi_i | \chi_k \rangle = D_k \delta_{ik} \quad (2)$$

where $k = 1, 2$; D_k are the normalization factors of the spin functions and $\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2 + \mathbf{s}_3 + \mathbf{s}_4$ is the total electron spin of the four-electron system.

The total wave function of the $^1S(L = 0)$ -state of the four-electron beryllium-like atom/ion is written in the form (see, e.g., [4], [5] and references therein)

$$\Psi_{L=0} = \psi_{L=0}(A; \{r_{ij}\}) \cdot \chi_1 + \phi_{L=0}(B; \{r_{ij}\}) \cdot \chi_2 \quad (3)$$

where $\psi_{L=0}(A; \{r_{ij}\})$ and $\phi_{L=0}(B; \{r_{ij}\})$ are the two independent radial parts (= spatial parts) of the total wave function. For the wave function, Eq.(3), one finds $\mathbf{S}^2\Psi = 0$ and $S_z\Psi = 0$, where $\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2 + \mathbf{s}_3 + \mathbf{s}_4$ is the total electron spin of the four-electron system. The radial parts $\psi_{L=0}(A; \{r_{ij}\})$ and $\phi_{L=0}(B; \{r_{ij}\})$ of the total wave function Eq.(3) in this work are represented in the form [6]

$$\psi_{L=0}(A; \{r_{ij}\}) = \mathcal{P}_1 \sum_{k=1}^{N_A} C_k \cdot \exp(-\sum_{ij} \alpha_{ij}^{(k)} r_{ij}^2) \quad (4)$$

$$\phi_{L=0}(B; \{r_{ij}\}) = \mathcal{P}_2 \sum_{k=1}^{N_B} \mathcal{C}_k \cdot \exp(-\sum_{ij} \beta_{ij}^{(k)} r_{ij}^2) \quad (5)$$

where N_A and N_B are the number of basis functions used, C_k and \mathcal{C}_k are the linear parameters of the variational expansions, Eq.(4) and Eq.(5), while $\{r_{ij}\}$ is the set of relative coordinates which are needed for complete description of five-body systems. The notations $\alpha_{ij}^{(k)}$ and $\beta_{ij}^{(k)}$ designate the non-linear parameters associated with the r_{ij} relative coordinate in the k -th basis function in the ψ and ϕ radial functions, respectively (see, Eqs.(4) - (5)). For all beryllium-like ions and atoms considered in this study the notation $\{r_{ij}\}$ stands for ten relative coordinates $r_{12}, r_{13}, r_{14}, r_{15}, r_{23}, r_{24}, r_{25}, r_{34}, r_{35}$ and r_{45} . The radial basis functions in Eqs.(4) - (5) are called the five-body gaussoids of the ten relative coordinates. This name was used in [6] where these basis functions were invented for nuclear few-body systems.

The main advantage of the radial function defined in Eqs.(4) - Eqs.(5) follows from the fact that the formulas for all matrix elements do not depend explicitly upon the total number of particles in the system. In other words, these formulas are essentially the same for three-, four-, five- and many-body systems and are discussed in the next Section.

The notations A and B in Eq.(4) and Eq.(5) mean that there are two different sets of non-linear parameters. Note that each of the basis functions in Eq.(4) and Eq.(5) contains ten non-linear parameters which are optimized independently. The summation over $(ij) = (ji)$ in the exponents of Eq.(4) and Eq.(5) is taken over all possible different pairs of particles. In general, the radial basis functions are not orthogonal to each other. The projectors \mathcal{P}_1 and \mathcal{P}_2 produce the trial wave functions with the correct permutation symmetry between all electrons (see below). The symbol L in Eq.(4) is used for the total angular momentum of the considered system. For the ground state of any Be-like system we always have $L = 0$ and the total electron spin of such states equals zero. Furthermore, the parity of these states in the four-electron systems is even. With respect to this, these states are often designated as the $^1S^e$ states, or 1^1S^e states.

For the triplet 3S -states in four-electron atomic systems one also finds the two independent spin functions $\chi_1 = \alpha\beta\alpha\alpha - \beta\alpha\alpha\alpha$ and $\chi_2 = 2\alpha\alpha\beta\alpha - \beta\alpha\alpha\alpha - \alpha\beta\alpha\alpha$. Note that there are, in fact, the two independent triplets of the spin functions, i.e. the total number of electron spin functions equals six ($6 = 2 \times 3$). The functions χ_1 and χ_2 mentioned above correspond to the values $S_e = 1$ and $(S_e)_z = 1$. By using the explicit form of these two spin functions one can construct the four remaining spin functions with $S_e = 1$ and $(S_e)_z = 0$ (two functions) and $S_e = 1$ and $(S_e)_z = -1$ (two functions). In actual calculations of internal atomic structure we can restrict ourselves to the use of the two spin functions χ_1 and χ_2 only. All six spin functions are needed only in some special cases, e.g., if an external magnetic field is present.

It is interesting to find that the total variational wave function Ψ of three-electron atoms and ions is also represented in the form of Eq.(3). In this case $\chi_1 = \alpha\beta\alpha - \beta\alpha\alpha$ and $\chi_2 = 2\alpha\alpha\beta - \beta\alpha\alpha - \alpha\beta\alpha$, while the two independent radial parts depend upon six relative coordinates $r_{12}, r_{13}, r_{23}, r_{14}, r_{24}, r_{34}$ (here the indexes 1, 2, 3 mean three electrons, while 4 stands for the nucleus). The radial basis functions can also be chosen in the form of Eq.(4) and Eq.(5), i.e. in the form of four-body gaussoids. In this case each of the radial basis functions contains six non-linear parameters. Note also that for each of the spin functions

we have $S^2\chi_i = \frac{3}{4}\chi_i$ and $(S)_z\chi_i = +\frac{1}{2}\chi_i$ (here $i = 1, 2$). The explicit constructions of the variational wave functions for three- and four-electron atomic systems is discussed below.

III. MATRIX ELEMENTS

Actual computation of the matrix elements with the four- and five-body gaussoids Eq.(4) and Eq.(5), is based on analytical formulas derived elsewhere (see, e.g., [6], [7]). It was mentioned already in [6] that the explicit expressions for all matrix elements needed for the solution of the Schrödinger equation depend upon the total number of particles A in the system as a numerical parameter. In other words, the expressions for matrix elements in three-electron systems coincide with the corresponding formulas for matrix elements obtained for four- and five- and many-electron systems. Moreover, in some few-body systems one of the electrons can be replaced by another particle, e.g., by μ^- muon, but such a replacement does not change the explicit formulas for matrix elements. Below, the symbol A designates the total number of particles (i.e. bodies) in the system. The A -particle atomic system includes the $(A - 1)$ -electron subsystem plus one heavy nucleus. The A -particle muonic atom/ion contains the $(A - 2)$ -electron subsystem, one negatively charged muon μ^- and one heavy nucleus.

The explicit formulas for all matrix elements needed in computations of the A -particle atomic systems can be presented in a very brief form with the use of the following compact notation

$$\langle \alpha | = \langle \alpha^{(k)} | = \exp(- \sum_{i>j=1}^A \alpha_{ij}^k \cdot r_{ij}^2) \quad \text{and} \quad | \beta \rangle = | \beta^{(\ell)} \rangle = \exp(- \sum_{i>j=1}^A \beta_{ij}^\ell \cdot r_{ij}^2) \quad (6)$$

where A is the total number of particles in the system. In this notation the symbols $| \beta \rangle$ and $| \alpha \rangle$ (or $\langle \alpha |$ and $\langle \beta |$) stand for the radial basis functions. These notations are different from the symbols α and β used in other Sections of this study to designate the spin-up and spin-down functions.

In the notation defined in Eq.(6) the overlap matrix element $\langle \alpha | \beta \rangle$ is written in the form

$$\langle \alpha | \beta \rangle = \langle \alpha^{(k)} | \beta^{(\ell)} \rangle = \pi^{\frac{3 \cdot (A-1)}{2}} \cdot D^{-\frac{3}{2}} \quad (7)$$

where D is the determinant of the $(A - 1) \times (A - 1)$ -matrix \hat{B} with the matrix elements

$$\begin{aligned} b_{ii} &= \sum_{j \neq i}^A (\alpha_{ij}^k + \beta_{ij}^\ell), \quad i \neq j = 1, 2, \dots, A - 1 \\ b_{ij} &= -(\alpha_{ij}^k + \beta_{ij}^\ell), \quad i \neq j = 1, 2, \dots, A - 1 \end{aligned} \quad (8)$$

In particular, the explicit expression for the (k, ℓ) matrix element of the overlap matrix \hat{S} in the case of $A = 5$ is the 4×4 matrix \hat{B} with matrix elements b_{ij} defined in Eq.(8). Analytical and/or numerical computations of the determinant of this matrix and all its first order derivatives is straightforward.

The formula for the appropriate matrix elements of the potential energy can be written in the form:

$$\sum_{(ij)} \langle \alpha | V(r_{ij}) | \beta \rangle = \frac{4}{\sqrt{\pi}} \langle \alpha | \beta \rangle \sum_{ij} \int_0^{+\infty} V\left(x \sqrt{\frac{D_{ij}}{D}}\right) \cdot \exp(-x^2) \cdot x^2 dx \quad (9)$$

where $D_{ij} = \frac{\partial D}{\partial \alpha_{ij}} = \frac{\partial D}{\partial \beta_{ij}}$, while $(ij) = (ji) = (12), (13), (23), (14), (24), (34)$ for the three-electron atom/ion ($A = 4$) and $(ij) = (ji) = (12), (13), (14), (15), \dots, (35), (45)$ for the four-electron atom/ion ($A = 5$). The explicit expressions for various interparticle potentials often used in bound state calculations can be found in [6]. The integral in the last formula is computed analytically in many actual cases, including the case of Coulomb, Yukawa-type, exponential, oscillator, and other potentials. The matrix elements of the kinetic energy take the form (in atomic units)

$$\langle \alpha | T | \beta \rangle = \frac{3}{2D} \left[\sum_{ijk=1}^A \frac{\alpha_{ik} \beta_{jk}}{m_k} (D_{ik} + D_{jk} - D_{ij}) \right] \langle \alpha | \beta \rangle \quad (10)$$

where $m_i (i = 1, 2, \dots, A)$ are the masses of the particles and $i \neq j \neq k$ in Eq.(10). The explicit formulas for matrix elements of other operators written in the basis of many-dimensional gaussoids can be found elsewhere (see, e.g., [6], [7]).

If all formulas needed for matrix elements of the potential and kinetic energies are known, then the solution of the incident Schrödinger equation is reduced to the following generalized eigenvalue problem

$$\sum_{\beta=1}^N (H_{\alpha,\beta} - E \cdot S_{\alpha,\beta}) C_\beta = 0 \quad (11)$$

for $\alpha = 1, \dots, N$, where N is the total number of basis functions used. Here $H_{\alpha,\beta} = T_{\alpha,\beta} + V_{\alpha,\beta} = \langle \alpha | T | \beta \rangle + \langle \alpha | V | \beta \rangle$ is the Hamiltonian matrix, while $T_{\alpha,\beta} = \langle \alpha | T | \beta \rangle$

and $V_{\alpha,\beta} = \langle \alpha | V | \beta \rangle$ are the matrices of the kinetic and potential energies, respectively. The $S_{\alpha,\beta} = \langle \alpha | \beta \rangle$ matrix in Eq.(11) is the overlap matrix, Eq.(7). For non-orthogonal basis sets the overlap matrix is a typical dense matrix, i.e. all elements of such a matrix differ, in general, from zero. Moreover, it can be shown that the overlap matrix $\langle \alpha | \beta \rangle$ is a symmetric, positively defined matrix. This means that all eigenvalues of the overlap matrix are positive.

IV. ANTISYMMETRIZATION OF THE TRIAL WAVE FUNCTIONS

Let us consider the antisymmetrization of the trial wave functions and related antisymmetrization of the corresponding matrix elements derived in the previous Section. As mentioned above the correct antisymmetrization is a central part of the construction of explicitly correlated, trial wave functions. In general, such a wave function depends upon all electron-nuclear and electron-electron coordinates. In two-electron atoms and ions the antisymmetrization of the total wave function is a trivial problem, since the wave function of the two-electron system is always represented as a product of a radial and two-electron spin functions. Moreover, only singlet and triplet spin functions are possible in any two-electron atom and/or ion. The singlet states have spin function $\chi_1 = \alpha\beta - \beta\alpha$, while triplet states have three spin functions $\chi_2^{(1)} = \alpha\alpha$, $\chi_2^{(2)} = \alpha\beta + \beta\alpha$, $\chi_2^{(3)} = \beta\beta$. For the singlet spin function one finds $S^2\chi_1 = 0$, $S_z\chi_1 = 0$, while for the triplet spin functions we have $S^2\chi_2^{(i)} = 1(1+1)\chi_2^{(i)} = 2\chi_2^{(i)}$ and $S_z\chi_2^{(i)} = \kappa_i\chi_2^{(i)}$, where $\kappa_1 = 1$, $\kappa_2 = 0$ and $\kappa_3 = -1$, respectively. Here and below S and S_z are the total electron spin of the system and its z -projection.

Note that the singlet χ_1 spin function is antisymmetric upon the electron variables. Therefore, its product with a symmetric radial function produces a function which is completely antisymmetric upon all electron variables. It is clear that such a function can be considered as a total wave function with the correct permutation symmetry between two electrons. For triplet states the corresponding radial function must be antisymmetric upon all electron (spatial) coordinates.

In contrast with two-electron systems, the antisymmetrization of three-electron wave functions is a significantly more complex process, since for the same spin state one finds not one, but a number of different independent spin functions. This statement is true

even for the doublet states with $S = \frac{1}{2}$ (i.e. $2S + 1 = 2$) and $S_z = \pm\frac{1}{2}$ in any three-electron atomic system. In actual computations, such spin functions are usually chosen to be orthogonal to each other. For instance, any variational expansion written for the doublet 2S -states in a three-electron atomic system must include the two independent spin functions $\chi_1 = \alpha\beta\alpha - \beta\alpha\alpha$ and $\chi_2 = 2\alpha\alpha\beta - \beta\alpha\alpha - \alpha\beta\alpha$. The total wave function for the ground doublet $1^2S(L=0)$ -state of the three-electron atomic system is written in the form (see, e.g., [9], [10])

$$\Psi_{L=0} = \psi_{L=0}(A; \{r_{ij}\})(\alpha\beta\alpha - \beta\alpha\alpha) + \phi_{L=0}(B; \{r_{ij}\})(2\alpha\alpha\beta - \beta\alpha\alpha - \alpha\beta\alpha) \quad (12)$$

where $\psi_{L=0}(A; \{r_{ij}\})$ and $\phi_{L=0}(B; \{r_{ij}\})$ are the two independent spatial parts (= radial parts) of the total wave function. The notations A and B mean that the two sets of non-linear parameters associated with ψ and ϕ are optimized independently.

Note that for each of these two spin functions χ_1 and χ_2 the two following equations are obeyed:

$$\mathbf{S}^2\chi_k = S(S+1)\chi_k = \frac{3}{4}\chi_k \quad , \quad (\mathbf{S})_z\chi_k = \frac{1}{2}\chi_k \quad (13)$$

where $k = 1, 2$ and $\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2 + \mathbf{s}_3$ is the total electron spin of the three-electron system, while \mathbf{S}_z is its z -projection. The conditions Eq.(13) indicate clearly that the two spin functions χ_1 and χ_2 are equally important in this variational method. Therefore, we cannot neglect any of these spin functions *a priori*. This means that in any of our calculations for three-electron atomic system we have to make appropriate use of the two different radial functions and two spin configurations χ_1 and χ_2 . The explicit construction of the trial wave functions for three-electron atomic systems with two independent spin functions is more complicated problem than in the case of one spin function and its solution is based on the method of projection operators is discussed below.

A. Three-electron atomic systems. Doublet states.

Suppose our trial wave function for a three-electron atomic system is written in the form of Eq.(12). In real applications, however, only those trial functions are accepted which have the correct permutation symmetry between all identical particles, i.e. electrons. This means that the two terms in the right-hand side of Eq.(12) must be completely antisymmetric upon spin and spatial coordinates of the three electrons, i.e. upon the indexes 1, 2 and 3 in our

notation. In other words, we must have $\hat{\mathcal{A}}_e \Psi = -\Psi$, where Ψ is given by Eq.(12) and $\hat{\mathcal{A}}_e$ is the three-particle (= electron) antisymmetrizer [11], [12]

$$\hat{\mathcal{A}}_e = \frac{1}{6}(\hat{e} - \hat{P}_{12} - \hat{P}_{13} - \hat{P}_{23} + \hat{P}_{123} + \hat{P}_{132}) \quad (14)$$

Here \hat{e} is the identity permutation, while \hat{P}_{ij} is the permutation of the i -th and j -th particles. Analogously, the operator \hat{P}_{ijk} is the permutation of the i -th, j -th and k -th particles. The same notations are used everywhere below in the text.

By using the three-particle antisymmetrizer, Eq.(14), we can construct a trial wave function of the correct permutation symmetry. In reality, we need the matrix elements with the correct permutation symmetry, rather than the wave function itself. Let us describe the approach which allows one to obtain properly symmetrized matrix elements. First, note that the expectation value of an arbitrary completely symmetric operator W is written in the form

$$\langle \hat{\mathcal{A}}_e \sum \psi_i(A_i; \{r_{ij}\}) \chi_i \mid W \mid \hat{\mathcal{A}}_e \sum \psi_j(A_j; \{r_{ij}\}) \chi_j \rangle \quad (15)$$

where χ_i are the spin functions ($i = 1, \dots, N_s$), where the $\hat{\mathcal{A}}_e$ operator is defined in Eq.(14). The spin functions χ_1 and χ_2 are assumed to be orthogonal to each other, i.e. $\langle \chi_i \mid \chi_j \rangle = \delta_{ij}$. The notations $\psi_i(A_i; \{r_{ij}\})$ stand for the corresponding radial functions which depend upon all relative coordinates $\{r_{ij}\}$ and non-linear parameters A_i . These radial functions can be arbitrary, i.e. they are not necessarily orthogonal to each other. The operator W is a differential operator written in the relative coordinates. It is assumed to be completely symmetric in respect to all inter-electron permutations.

Now note that completely symmetric operator W commutes with the $\hat{\mathcal{A}}_e$ operator, Eq.(14). Moreover, the operator $\hat{\mathcal{A}}_e$ is an orthogonal projector [13], i.e. $(\hat{\mathcal{A}}_e)^2 = \hat{\mathcal{A}}_e$ and $(\hat{\mathcal{A}}_e)^* = \hat{\mathcal{A}}_e$, where the symbol B^* means the operator conjugate to the operator B . If the operator W does not depend upon spin variables, then by using these properties of the $\hat{\mathcal{A}}_e$ operator one can reduce the formula, Eq.(15), to the following form

$$\sum_i \sum_j \langle \psi_i(A_i; \{r_{ij}\}) \mid W \mid \hat{\mathcal{A}}_e \psi_j(A_j; \{r_{ij}\}) \rangle \langle \chi_i \mid \hat{\mathcal{A}}_e \mid \chi_j \rangle \quad (16)$$

This expectation value can be re-written into another form with the use of the following matrix notation

$$[\Theta(W)]_{ij} = \langle \chi_i \mid \hat{\mathcal{A}}_e \mid \chi_j \rangle [W \hat{\mathcal{A}}_e]_{ij} \quad (17)$$

where $[\dots]_{ij}$ designates the (ij) –matrix element of the corresponding matrix. The matrix elements of this operator ($\Theta(W)$) computed on any basis set of spatial three-electron wave functions have the correct permutation symmetry between all identical particles (electrons). The dimension of the $[\Theta(W)]_{ij}$ matrix equals to the number of spin functions used in calculations.

First, let us compute the matrix elements of the $\hat{\mathcal{A}}_e$ operator, where $\hat{\mathcal{A}}_e$ designates the complete three-particle antisymmetrizer, Eq.(14). Based on Eq.(17) this operator can be written in the form $\Theta(\hat{e})$, where \hat{e} is the unit operator. Note that operator $\hat{\mathcal{A}}_e$, Eq.(14), is written in the form

$$\hat{\mathcal{A}}_e = \sum_{abc} s_{abc} \hat{P}_{abc} \quad (18)$$

where s_{abc} is an integer number, while \hat{P}_{abc} are the interparticle permutations in the system of three identical particles (see Eq.(14)). The sum in Eq.(18) is computed over all interparticle permutations possible in three-body systems, Eq.(14). The (ij) –matrix element of the $\hat{\mathcal{A}}_e$ operator in our basis is

$$[\hat{\mathcal{A}}_e]_{ij} = \sum_{abc} s_{abc} \langle \chi_i | \hat{P}_{abc} | \chi_j \rangle \hat{P}_{abc} \quad (19)$$

In the case of the (ij) –matrix element of the $\Theta(W)$ operator one finds

$$[\Theta(W)]_{ij} = \sum_{abc} s_{abc} \langle \chi_i | \hat{P}_{abc} | \chi_j \rangle W \hat{P}_{abc} = W \left[\sum_{abc} s_{abc} \langle \chi_i | \hat{P}_{abc} | \chi_j \rangle \hat{P}_{abc} \right] \quad (20)$$

Note that both the expectation value $\langle \chi_i | \hat{P}_{abc} | \chi_j \rangle$ and s_{abc} are the integers for all abc , while the operator P_{abc} is a projector which acts on the spatial coordinates of three electrons ($a \rightarrow b \rightarrow c$). In other words, the $\hat{\mathcal{A}}_e$ operator is represented as the finite sum of all spatial permutations \hat{P}_{abc} with integer coefficients equal to the products of s_{abc} , Eq.(18), and the $\langle \chi_i | \hat{P}_{abc} | \chi_j \rangle$ expectation values. The computation of all expectation values $\langle \chi_i | \hat{P}_{abc} | \chi_j \rangle = \langle \chi_i | \hat{P}_{abc} \chi_j \rangle$ can be considered as the integration over electron spin coordinates.

Based on Eq.(20) we can introduce the following operator \mathcal{P}

$$\mathcal{P} = \mathcal{D} \sum_{abc} s_{abc} \langle \chi_i | \hat{P}_{abc} | \chi_j \rangle \hat{P}_{abc} \quad (21)$$

where \mathcal{D} is the normalization constant. The numerical value of \mathcal{D} in Eq.(21) is determined by the idempotency of the \mathcal{P} operator, i.e. $\mathcal{P}^2 = \mathcal{P}$. The explicit use of this operator

substantially simplifies all following formulas. For instance, the (α, β) -matrix element of any arbitrary completely symmetric operator W can be written in the form

$$\langle \mathcal{P}\alpha | W | \mathcal{P}\beta \rangle = \langle \alpha | \mathcal{P}W\mathcal{P} | \beta \rangle = \langle \alpha | W\mathcal{P} | \beta \rangle = \langle \alpha | W | \mathcal{P}\beta \rangle \quad (22)$$

where α and β are non-symmetric basis functions. This matrix element has the correct permutation symmetry between all electrons. Moreover, all expectation values constructed with the use of these matrix elements, Eq.(22), also have the correct permutation symmetry between all electrons. This is the main advantage of constructing the orthogonal spatial projector \mathcal{P} in explicit form.

In actual computations of the doublet 2S -states in three-electron atomic systems after the integration over electron spin coordinates, one finds the four following spatial projectors

$$\mathcal{P}_{\psi\psi} = \frac{1}{2\sqrt{3}}(2\hat{e} + 2\hat{P}_{12} - \hat{P}_{13} - \hat{P}_{23} - \hat{P}_{123} - \hat{P}_{132}) \quad (23)$$

$$\mathcal{P}_{\psi\phi} = \frac{1}{2}(\hat{P}_{13} - \hat{P}_{23} + \hat{P}_{123} - \hat{P}_{132}) \quad (24)$$

$$\mathcal{P}_{\phi\psi} = \frac{1}{2}(\hat{P}_{13} - \hat{P}_{23} + \hat{P}_{123} - \hat{P}_{132}) \quad (25)$$

$$\mathcal{P}_{\phi\phi} = \frac{1}{2\sqrt{3}}(2\hat{e} - 2\hat{P}_{12} + \hat{P}_{13} + \hat{P}_{23} - \hat{P}_{123} - \hat{P}_{132}) \quad (26)$$

Here the indexes ψ and ϕ correspond to the notations for radial functions used in Eq.(12). Each of these projectors produces matrix elements between the two radial basis functions from Eq.(12) with the correct permutation symmetry. Note that the two projectors $\mathcal{P}_{\psi\phi}$ and $\mathcal{P}_{\phi\psi}$ written above coincide with each other. It can also be shown that the three projectors $\mathcal{P}_{\psi\psi}$, $\mathcal{P}_{\psi\phi}$ and $\mathcal{P}_{\phi\phi}$ are orthogonal to each other. In actual computations only the upper triangles of the Hamiltonian and overlap matrices are used. Therefore, only the three projectors $\mathcal{P}_{\psi\psi}$, $\mathcal{P}_{\psi\phi}$ and $\mathcal{P}_{\phi\phi}$ are important in computations of the bound doublet 2S -states in all three-electron atomic systems.

The approach described above allows one to construct the spatial parts of the total variational wave functions with the correct permutation symmetry between all identical particles in the three-electron atomic system. In our previous work we have also found (see, e.g., [2], [5]) that the same approach works perfectly for all four-, five- and many-electron systems. Moreover, the symmetry of the electron spin functions can also be different, e.g., for the singlet and triplet states in four-electron systems. Below, the variational wave functions for the singlet and triplet states in the four-electron atomic systems are explicitly

constructed. The explicit formulas for the spatial parts of trial wave functions are derived with the use of the corresponding spatial projectors.

B. Four-electron atomic systems. Singlet states.

Numerical computations of the bound states in four-electron atomic systems include the non-trivial step of antisymmetrization of all electronic variables, i.e. variables 1, 2, 3 and 4 in the trial wave function Ψ . The variational wave function Ψ of any singlet $^1S(L=0)$ -state in four-electron atomic systems is represented in the form of Eq.(27), i.e.

$$\begin{aligned}\Psi_{L=0} = & \psi_{L=0}(A; \{r_{ij}\})(\alpha\beta\alpha\beta + \beta\alpha\beta\alpha - \beta\alpha\alpha\beta - \alpha\beta\beta\alpha) \\ & + \phi_{L=0}(B; \{r_{ij}\})(2\alpha\alpha\beta\beta + 2\beta\beta\alpha\alpha - \beta\alpha\alpha\beta - \alpha\beta\beta\alpha - \beta\alpha\beta\alpha - \alpha\beta\alpha\beta)\end{aligned}\quad (27)$$

where $\psi_{L=0}(A; \{r_{ij}\})$ and $\phi_{L=0}(B; \{r_{ij}\})$ are the two independent spatial parts (= radial parts) of the total four-electron wave function. The notations A and B mean that the two sets of non-linear parameters associated with ψ and ϕ are optimized independently. Such a trial wave function must be antisymmetric upon all electron variables (or variables 1, 2, 3 and 4 in our notations), i.e. $\hat{\mathcal{A}}_e \Psi = -\Psi$, where

$$\begin{aligned}\hat{\mathcal{A}}_e = & \hat{e} - \hat{P}_{12} - \hat{P}_{13} - \hat{P}_{23} - \hat{P}_{14} - \hat{P}_{24} - \hat{P}_{34} + \hat{P}_{123} + \hat{P}_{132} + \hat{P}_{124} + \hat{P}_{142} + \hat{P}_{134} \\ & + \hat{P}_{143} + \hat{P}_{234} + \hat{P}_{243} - \hat{P}_{1234} - \hat{P}_{1243} - \hat{P}_{1324} - \hat{P}_{1342} - \hat{P}_{1423} - \hat{P}_{1432} + \hat{P}_{12} \cdot \hat{P}_{34} \\ & + \hat{P}_{13} \cdot \hat{P}_{24} + \hat{P}_{14} \cdot \hat{P}_{23}\end{aligned}\quad (28)$$

is the complete four-particle antisymmetrizer. Here \hat{e} is the identity permutation, while \hat{P}_{ij} is the permutation of the particles i and j . Analogously, the operators \hat{P}_{ijk} and \hat{P}_{ijkl} are the permutations of the particles i, j, k and i, j, k, l , respectively.

By using the procedure described in the previous Section we can find the explicit formulas for the corresponding spatial projectors. In fact, by using the explicit form of the trial wave function Ψ constructed for singlet states in four-electron systems, Eq.(27), and by integrating over electron spin coordinates one finds the four following spatial projectors:

$$\begin{aligned}\mathcal{P}_{\psi\psi} = & \frac{1}{4\sqrt{3}} \left(2\hat{e} + 2\hat{P}_{12} - \hat{P}_{13} - \hat{P}_{23} - \hat{P}_{14} - \hat{P}_{24} + 2\hat{P}_{34} + 2\hat{P}_{12}\hat{P}_{34} + 2\hat{P}_{13}\hat{P}_{24} + 2\hat{P}_{14}\hat{P}_{23} \right. \\ & - \hat{P}_{123} - \hat{P}_{132} - \hat{P}_{124} - \hat{P}_{142} - \hat{P}_{134} - \hat{P}_{143} - \hat{P}_{234} - \hat{P}_{243} - \hat{P}_{1234} - \hat{P}_{1243} \\ & \left. + 2\hat{P}_{1324} - \hat{P}_{1342} - \hat{P}_{1432} + 2\hat{P}_{1423} \right)\end{aligned}\quad (29)$$

$$\mathcal{P}_{\psi\phi} = \frac{1}{4} \left(\hat{P}_{13} - \hat{P}_{23} - \hat{P}_{14} + \hat{P}_{24} + \hat{P}_{123} - \hat{P}_{132} - \hat{P}_{124} + \hat{P}_{142} + \hat{P}_{134} - \hat{P}_{143} - \hat{P}_{234} + \hat{P}_{243} \right. \\ \left. + \hat{P}_{1234} - \hat{P}_{1243} - \hat{P}_{1342} + \hat{P}_{1432} \right) \quad (30)$$

$$\mathcal{P}_{\phi\psi} = \mathcal{P}_{\psi\phi} \quad (31)$$

$$\mathcal{P}_{\phi\phi} = \frac{1}{4\sqrt{3}} \left(2\hat{e} - 2\hat{P}_{12} + \hat{P}_{13} + \hat{P}_{23} + \hat{P}_{14} + \hat{P}_{24} - 2\hat{P}_{34} + 2\hat{P}_{12}\hat{P}_{34} + 2\hat{P}_{13}\hat{P}_{24} + 2\hat{P}_{14}\hat{P}_{23} \right. \\ \left. - \hat{P}_{123} - \hat{P}_{132} - \hat{P}_{124} - \hat{P}_{142} - \hat{P}_{134} - \hat{P}_{143} - \hat{P}_{234} - \hat{P}_{243} + \hat{P}_{1234} + \hat{P}_{1243} \right. \\ \left. - 2\hat{P}_{1324} + \hat{P}_{1342} + \hat{P}_{1432} - 2\hat{P}_{1423} \right) \quad (32)$$

In reality, since $\mathcal{P}_{\psi\phi} = \mathcal{P}_{\phi\psi}$, one needs to use only three such operators $\mathcal{P}_{\psi\psi}$, $\mathcal{P}_{\psi\phi}$ and $\mathcal{P}_{\phi\phi}$. The use of these three projectors for matrix elements allows one to produce the matrix elements which have the correct permutation structure between all four identical particles (electrons). Note that all such matrix elements are computed only between the corresponding spatial basis functions and do not include any spin function. The explicit formulas for the complete set of singlet spatial projectors for four-electron atomic systems, Eqs.(29) - (32), have not been presented in previous publications. First bound state computations of four-electron atomic systems with the use of completely correlated wave functions were performed by Sims and Hagström [8]. Since then many authors have conducted such calculations for singlet states in various four-electron systems (see, e.g., [5] and references therein).

C. Four-electron atomic systems. Triplet states.

The trial wave function of the triplet 3S -state in the four-electron atomic system can also be represented in the form with the two independent spin functions $\chi_1 = \alpha\beta\alpha\alpha - \beta\alpha\alpha\alpha$ and $\chi_2 = 2\alpha\alpha\beta\alpha - \beta\alpha\alpha\alpha - \alpha\beta\alpha\alpha$. The variational expansion takes the form

$$\Psi = \psi_{L=0}(A; \{r_{ij}\}) \cdot (\alpha\beta\alpha\alpha - \beta\alpha\alpha\alpha) + \phi_{L=0}(B; \{r_{ij}\}) \cdot (2\alpha\alpha\beta\alpha - \beta\alpha\alpha\alpha - \alpha\beta\alpha\alpha) \quad (33)$$

where $\psi_{L=0}(A; \{r_{ij}\})$ and $\phi_{L=0}(B; \{r_{ij}\})$ are the radial parts (also called the spatial part) of the total wave function. Here the notation $\{r_{ij}\}$ designates the complete set of fifteen interparticle (spatial) coordinates, while the symbol A and B mean the corresponding sets of non-linear parameters. Optimization of non-linear parameters in the A - and/or B -sets is performed independently from each other. The trial wave function, Eq.(34), contains two electron spin functions χ_1 and χ_2 which correspond to the $S = 1$ and $S_z = 1$ values,

where S and S_z are the eigenvalues of the total electron spin and its z -projection, i.e. $\mathbf{S}^2\chi_i = S(S+1)\chi_i$ and $\mathbf{S}_z\chi_i = S_z\chi_i$.

For triplet states by using the explicit form of the χ_1 and χ_2 functions one can easily find the four other spin functions which correspond to the $S = 1$ and $S_z = 0$ and $S = 1$ and $S_z = -1$ values. For instance, in the case of $\chi_1 = \chi_1^{(+1)}$ spin function the two spin functions $\chi_1^{(0)} = \alpha\beta\alpha\beta + \alpha\beta\beta\alpha - \beta\alpha\alpha\beta - \beta\alpha\beta\alpha$ and $\chi_1^{(-1)} = \alpha\beta\beta\beta - \beta\alpha\beta\beta$ correspond to the $S = 1, S_z = 0$ and $S = 1, S_z = -1$ values, respectively. The three spin functions $\chi_1^{(+1)}, \chi_1^{(0)}, \chi_1^{(-1)}$ form a regular triplet of spin functions. An analogous triplet of spin functions can be constructed for the χ_2 spin function. To describe experimental situations with no external magnetic field present we need to use the spin functions associated with one value of S_z , say, $S_z = 1$. Thus in this work we shall always choose $\chi_1 = (\alpha\beta - \beta\alpha)\alpha\alpha = \alpha\beta\alpha\alpha - \beta\alpha\alpha\alpha$ and $\chi_2 = 2\alpha\alpha\beta\alpha - \beta\alpha\alpha\alpha - \alpha\beta\alpha\alpha$ (see Eq.(33) above).

In calculations with such a trial wave function, Eq.(33), one needs to know the explicit formulas for all three radial (or spatial) projectors $\mathcal{P}_{\psi\psi}$, $\mathcal{P}_{\phi\psi}(= \mathcal{P}_{\psi\phi})$ and $\mathcal{P}_{\phi\phi}$. However, numerical calculations using a wave function with two spin functions are computationally intensive and were not attempted in the current study. Accordingly, we did not attempt to derive the associated projectors. Instead, we performed some computations of the triplet states in four-electron atomic systems with the use of one spin function $\chi_1 = \chi_1^{(+1)} = \alpha\beta\alpha\alpha - \beta\alpha\alpha\alpha$ only. The variational expansion Eq.(33) is now written in the form

$$\Psi = \psi_{L=0}(A; \{r_{ij}\}) \cdot (\alpha\beta - \beta\alpha)\alpha\alpha = \psi_{L=0}(A; \{r_{ij}\}) \cdot (\alpha\beta\alpha\alpha - \beta\alpha\alpha\alpha) \quad (34)$$

Now, we need to obtain the spatial part of the total wave function with the correct permutation symmetry between all identical particles 1, 2, 3 and 4 (electrons). The corresponding spatial projector is obtained in this work by calculating the explicit expression for the following spin expectation value

$$\mathcal{P}_{\psi\psi} = \mathcal{C} \sum_{abcd} s_{abcd} \langle (\alpha\beta - \beta\alpha)\alpha\alpha | \hat{P}_{abcd} | (\alpha\beta - \beta\alpha)\alpha\alpha \rangle \hat{P}_{abcd} \quad (35)$$

where \mathcal{C} is the normalization factor, while the integers s_{abcd} are defined from the explicit form of the complete four-particle (or four-electron) antisymmetrizer $\hat{\mathcal{A}}_e$ given in Eq.(28). After some algebra one finds the explicit formula for the corresponding spatial projector

$$\begin{aligned} \mathcal{P}_{\psi\psi} = \frac{1}{2\sqrt{6}} & \left(2\hat{e} + 2\hat{P}_{12} - \hat{P}_{13} - \hat{P}_{23} - \hat{P}_{14} - \hat{P}_{24} - 2\hat{P}_{34} - 2\hat{P}_{12}\hat{P}_{34} - \hat{P}_{123} - \hat{P}_{124} \right. \\ & \left. - \hat{P}_{132} - \hat{P}_{142} + \hat{P}_{134} + \hat{P}_{234} + \hat{P}_{243} + \hat{P}_{143} + \hat{P}_{1432} + \hat{P}_{1234} + \hat{P}_{1243} + \hat{P}_{1342} \right) \end{aligned} \quad (36)$$

This projector creates the spatial part of an arbitrary matrix element needed in bound state computations of the triplet 3S -states in an arbitrary four-electron atomic system. Such a matrix element has the correct permutation symmetry among all four identical particles (electrons). Explicit formulas for the spatial projectors which correspond to the triplet states have not been published previously.

By using the formulas presented above one can perform accurate computations of the triplet bound states in various four-electron atomic systems. As follows from our results of such calculations (see, e.g., [2]) the method described above allows one to determine various expectation values in four-electron atomic systems to relatively high numerical accuracy. In particular, such expectation values can be computed for all positive and negative powers of relative coordinates r_{ij} . In general, the expectation value of any regular function of the ten relative coordinates r_{ij} can be computed to very good numerical accuracy. Analogous expectation values which contain delta-functions of the relative coordinates and their products with the regular functions of the relative coordinates also do not present any problem for numerical computations. Real problems arise in computations of expectation values which include products of delta-functions with the corresponding electron spin functions, e.g., $\langle \alpha_i \delta_{Ni} \rangle$ and $\langle \alpha_i \beta_j \delta_{Ni} \delta_{Nj} \rangle$, where N designates the nucleus, while i means i -th electron. The first expectation value $\langle \alpha_i \delta_{Ni} \rangle$ represents the single-electron density of α -electrons on the atomic nucleus. Analogous expectation values can be computed in the case of β -electrons. A very poor convergence of similar expectation values means that another spin function must be included in computations. In Eq.(33) such a spin function is called the second (electron) spin function χ_2 .

V. GENERALIZATION TO THE FIVE- AND SIX-ELECTRON ATOMIC SYSTEMS.

The method described above allows one to construct the properly antisymmetrized trial functions for three- and four-electron atomic systems. Formally, our method can be generalized to the five, six and many-electron atomic systems. However, its direct generalization is very difficult, since the proper antisymmetrization of the trial basis functions and their linear combinations becomes extremely difficult in the case of many-electron atoms with $A - 1 \geq 5$ electrons, i.e. for $A \geq 6$. Here and everywhere below, A is the total number of

particles in the system, while $A - 1$ is the total number of electrons. This means to construct the trial wave functions for five-, six- and many-electron atoms one needs to apply $A!(\geq 120)$ different interparticle permutations to the non-symmetrized basis function. The presence of a very large number of terms in each wave function drastically complicates the explicit expressions for the spatial projectors mentioned above. For instance, such a spatial projector constructed for the B-atom (five-electron atom) must include 120 different terms. Some of these terms can be equal zero identically, but in any case the total number of remaining terms is still very large. Therefore, it is important to develop some effective methods which can be used to operate with a very large number of terms in the trial wave functions. Our current hopes rely on the two following methods. The first approach is based on the use of various symbolic-algebra computational platforms such as Maple [16]. In this approach all integrations over spin variables can be performed analytically. The expressions for all spatial projectors are never written explicitly, but they are used internally by this computational platform. Note also that for some basis sets the action of any interparticle permutation $\hat{P}_{abc\dots}$ on the basis wave functions is reduced to the permutation of the corresponding non-linear parameters in these functions. In particular, this is the case for variational expansion defined by Eqs.(4) and (5). This means that actual permutations of the non-linear parameters in the basis wave functions, Eqs.(4) and (5), can always be applied instead of the permutation of the relative coordinates. This drastically simplifies the explicit construction of the completely symmetrized trial wave functions. The permutation of the non-linear parameters in the basis wave functions can be combined with the analytical integration over spin variables in the total wave function. This can be used in the future methods.

The second approach is based on the relations which exist for the spin functions in three-, four- and many-electron systems. For instance, the second spin function χ_2 used in numerical computations of the triplet states of four-electron systems (see above) is obtained from the χ_2 spin function known for the doublet states in three-electron systems. Formally, we can write $\chi_2(1, 2, 3, 4) = \chi_2(1, 2, 3)\alpha(4)$, where $\alpha(4)$ is the spin function of the additional (= fourth) electron, while symbols $(1,2,3,4)$ and $(1,2,3)$ designate the systems of four and three electrons, respectively. The notation $\chi_2(1, 2, 3)$ stands for the second spin function of the doublet state in three-electron system, while $\chi_2(1, 2, 3, 4)$ means the second triplet spin function of the four-electron system. Analogous relation exists between another (first) triplet spin function of the four-electron atomic systems, $\chi_1(1, 2, 3, 4)$, and $\chi_1(1, 2, 3)$ used above

(see, e.g., Eq.(12)) for the doublet states in three-electron atoms/ions. By studying this and other similar relations between spin functions we can find some useful connections between the spatial projectors constructed for three- and four-electron systems. This approach can also simplify methods and algorithms which must be developed in the future for systems 5 or more electrons.

VI. NUMERICAL RESULTS

To illustrate our method in applications to actual three- and four-electron atomic systems let us briefly describe the results of variational computations of bound states in the three-electron Be^+ ion in its 1^2S -state and four-electron Be atom in its 1^1S - and 2^3S -states. For simplicity all nuclear masses were assumed to be infinite in such calculations. A separate group of calculations have been performed for the 2^3S -electron state in the six-body oxygen-muonic ion $\text{O}^{8+}\mu^-e_4^-$, where μ^- is the negatively charged muon. This positively charged ion ($q = +3$) is a well bound atomic system which contains the composite ‘nucleus’ ($\text{O}^{8+} + \mu^-$) with overall ‘nuclear’ charge $+7$ and four atomic electrons. Below, we consider the ^{16}O nucleus only. In our calculations of the $\text{O}^{8+}\mu^-e_4^-$ ion we used $M = 29156.9457 m_e$ for the nuclear mass of the oxygen-16 nucleus and $m_\mu = 206.768262 m_e$ [14], [15].

Numerical results of our computations can be found in Table I where one finds the total energies E and some other bound state properties expressed in atomic units, where $\hbar = 1$, $m_e = 1$ and $e = 1$. The electron state of each atomic system is shown in the following brackets. In the case of the $\text{O}^{8+}\mu^-e_4^-$ ion the notation 2^3S_e stands for the 2^3S_e -triplet electron state in this system. The muonic quasi-nucleus $\text{O}^{8+} + \mu^-$ is in its ground 1^1S -state. This is always assumed, but not shown in our notation. Note also that for bound state properties presented in Table I the index e means the electron, while the index N denotes the atomic nucleus. For each energy shown in Table I only 9 decimal digits are presented. In general, optimization of the non-linear parameters in variational expansion Eqs.(4) and (5) always decreases the total energies. On the other hand, small variations in a few last decimal digits are not critically important for our present purposes.

As follows from Table I our method provides very good numerical accuracy for doublet states in three-electron atoms and ions. On the other hand, this method also works perfectly for singlet and triplet four-electron atomic systems. It is very likely that the analogous

procedure can be developed for five-, six- and many-electron atomic systems. However, for atomic systems with five and more electrons one finds a number of additional problems and direct generalization of our method is very difficult (see discussion in the previous Section).

Note also that the overall convergence rates of the radial variational expansion, Eqs.(4) - (5), for three- and four-electron atomic systems are comparable with each other. It seems to be very strange, but we need to remember that the number of non-linear parameters in each basis function rapidly increases as the total number of bodies A in system increases. For four-electron atomic systems each of these basis function contains 10 non-linear parameters (each of them varied independently), while for three-electron atomic systems one finds only 6 such parameters in each basis function. Briefly, this means that the overall ‘flexibility’ of the four-electron trial function is comparable with the analogous ‘flexibility’ of the three-electron trial functions.

VII. CONCLUSION

We have considered the problem of accurate computations of bound states in three- and four-electron atomic systems. The method developed in this study allows one to construct variational wave functions for an arbitrary bound state in three- and four-electron atomic systems. All such trial wave functions have the correct permutation symmetry (with respect to all permutations of identical particles, i.e. electrons). It is important to note that in our method the total number of independent spin functions can be varied. Numerical computations can start with the use of one electron spin function only. The second spin function can be introduced later to improve the overall convergence of the results. Our procedure can be generalized to bound states with the non-zero angular momentum L . Such a generalization is straightforward, but it requires extensive use of additional notations, application of special methods developed in theory of angular momentum and substantial explanations. Variational calculations of the bound $P(L = 1)$ –states in five-electron atomic systems will be considered in our next study. The ground state of the B-atom is the $P(L = 1)$ –state.

Our method is based on explicit constructions of the total wave functions for various bound states in three- and four-electron atomic systems. The unified procedure has been applied to an example of each type of system. The central part of the procedure is the construction of spatial projectors with the correct permutation symmetry between all iden-

tical particles (electrons). This method was originally developed for three-electron atomic systems by Larsson [9] (see also [10]). We generalized this procedure to the cases when a number of different spin functions are used in computations. In addition, we have constructed spatial projectors needed in calculations of the singlet and triplet bound states in four-electron atomic systems. Currently, the total energies and other properties of bound states in four-electron atomic systems can be determined to the accuracy which is better than the accuracy of old bound state calculations performed for two-electron atomic systems [17]. In general, by using various optimization strategies for non-linear parameters from the trial wave functions one can obtain very accurate variational energies and highly accurate wave functions. Such wave functions can be used in the following accurate computations of different bound state properties, including various relativistic and QED corrections.

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TABLE I: The non-relativistic energies and other properties determined for the S -states in some three- and four-electron atoms, ions and muonic ions (in atomic units).

	$\text{Be}^+ (1^2S)$	$\text{Be} (1^1S)$	$\text{Be} (2^3S)$	$\text{O}^{8+}\mu^-e_4^- (2^3S_e)$
E	-14.3247627	-14.6673323	-14.4300595	-6619.33457
$\langle r_{eN}^{-1} \rangle$	2.65796	2.10684	2.03603	4.77655
$\langle r_{ee}^{-1} \rangle$	1.08200	0.72912	0.61933	1.26072
$\langle r_{eN} \rangle$	1.03379	1.49297	2.63085	0.98798
$\langle r_{ee} \rangle$	1.75565	2.54516	4.70847	2.43483